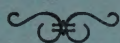


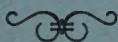
CCHEMICAL Constitution and Color
Among the Columbia Yellow Group
of Dyes, Syntheses of New Thiazole Dye
Intermediates and Studies on Diamino-
Thiosulfuric Acids.



L. C.

DISSERTATION

Submitted in Partial Fulfillment of the Requirements
for the Degree of Doctor of Philosophy
in the Faculty of Pure Science
Columbia University



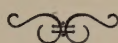
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1929

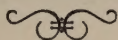
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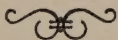


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By
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New York City

1929

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To

THOMAS DAVIDSON CHRISTIE, D.D., L.L.D.

Founder and Former President of St. Paul's College

and

Mrs. CARMELITE BREWER CHRISTIE

who strived to build a new century upon an old century

This Thesis is Gratefully Dedicated.

ACKNOWLEDGMENT

It is a great pleasure to express my indebtedness and appreciation to Professor Marston Taylor Bogert for the suggestion of this investigation and for his valuable assistance and supervision.

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CHEMICAL CONSTITUTION AND COLOR AMONG THE COLUMBIA YELLOW GROUP OF DYES, SYNTHESSES OF NEW THIAZOLE DYE INTERMEDIATES AND STUDIES ON DIAMINO-THIOSULFURIC ACIDS

ABSTRACT OF DISSERTATION

The object of the following investigation was to further our knowledge regarding chemical constitution and color among a new series of the Columbia Yellow group of dyes. In order to attain this object a new group of dye intermediates, analogous in structure to the important thiazole dye intermediate dehydrothio-p-toluidine, were prepared. Some of these new intermediates related to dehydrothio-p-toluidines are as follows:

1. 2-(o-aminophenyl)-5-methyl-6-amino-benzothiazole
2. 2-(p-aminophenyl)-5-methyl-6-amino-benzothiazole
3. 2-(o:p-diaminophenyl)-5-methyl-6-amino-benzothiazole

Due to the difficulty in obtaining a fair quantity of the desired products to carry the above project to completion, and for the reason that we may be able to compare the color and the properties of the products obtained during this investigation with the structurally analogous products obtained by the previous investigators in this field, the first and second of the above intermediates were converted into the Columbia Yellow type of dyes by sulphonating them and oxidizing the sulphonated products in an alkaline medium by means of sodium hypochlorite solution. The dyes thus obtained were found to be decidedly different from Columbia Yellow dyes obtained by previous investigators from 2-(p-aminophenyl)-6-methyl-benzothiazole, 2-(p-aminophenyl)-5-methyl-benzothiazole, and 2-(p-aminophenyl)-7-methyl-benzothiazole dye intermediates. The dyes obtained from the latter intermediates are all yellow in shade and hardly distinguishable one from another. The dyes obtained during this investigation from 2-(o-amino-phenyl)-5-methyl-6-amino-benzothiazole and 2-(p-amino-

phenyl)-5-methyl-6-amino-benzothiazole are shiny coal black in physical appearance and possess forms resembling needle shaped crystals. These new dyes dyed unbleached cotton directly, imparting to it a deep orange-tan color and are fast to alkalis and acids. Of the two dyes the one resulting from 2-(p-aminophenyl) isomer manifested slightly deeper shade.

The presence of free amino groups in the new dyes was studied by diazotizing and coupling them with β -naphthol. The resulting product dyed unbleached cotton directly, imparting to it a fast tan color possessing a red tint. The presence of the free amino groups in the new dyes offers important possibilities in producing new fast shades by coupling them with various coupling reagents.

It was also observed that of the corresponding homologues of the two groups of thiazole dye intermediates those possessing an additional amino group in the thiazole portion of the molecule were more intense in color and fluorescence. There was also noticed a marked difference in color among the various members of the new group of dehydro-thio-paratoluidines mentioned above. Previous investigators do not report any marked difference in color among the isomers prepared by them of the corresponding group of dehydrothio-p-toluidines which lack the amino group in the thiazole nucleus. Differences of the same magnitude were also observed between the two groups of nitro derivatives of dehydrothio-p-toluidines.

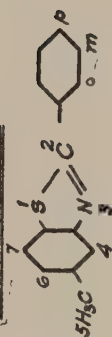
These results emphasize the important influence played upon the properties of thiazole dyes and dye intermediates by the introduction of an additional amino group in position six in the thiazole nucleus and by shifting the amino group in the 2-(phenyl) portion of the molecule to various positions.

To obtain the above mentioned intermediates p-toluylenediamine was used as the starting material. Due to the unavailability of a suitable sulphur derivative of this diamine which could be converted to the new homologues of dehydrothio-p-toluidines, it was necessary to convert the diamine into diamino-thiosulfuric acid. This acid on condensing with nitrobenzaldehydes in glacial acetic acid yielded the desired products. Diamine and alkylated diamino-thiosulfuric acids have been used by Bernthsen and others as starting materials for the preparation of the important series of methylene blue and methylene red group of dyes. In view of the above, we thought it advisable to study the properties of this new diamino-thiosulfuric acid by determining its ionization constant. To this end potentiometric titrations were carried out and the results plotted graphically in the form of titration curves. From these results the ionization constant of p-toluylenediamine-thiosulfuric acid was calculated to be 5.56×10^{-6} , at 25°C .

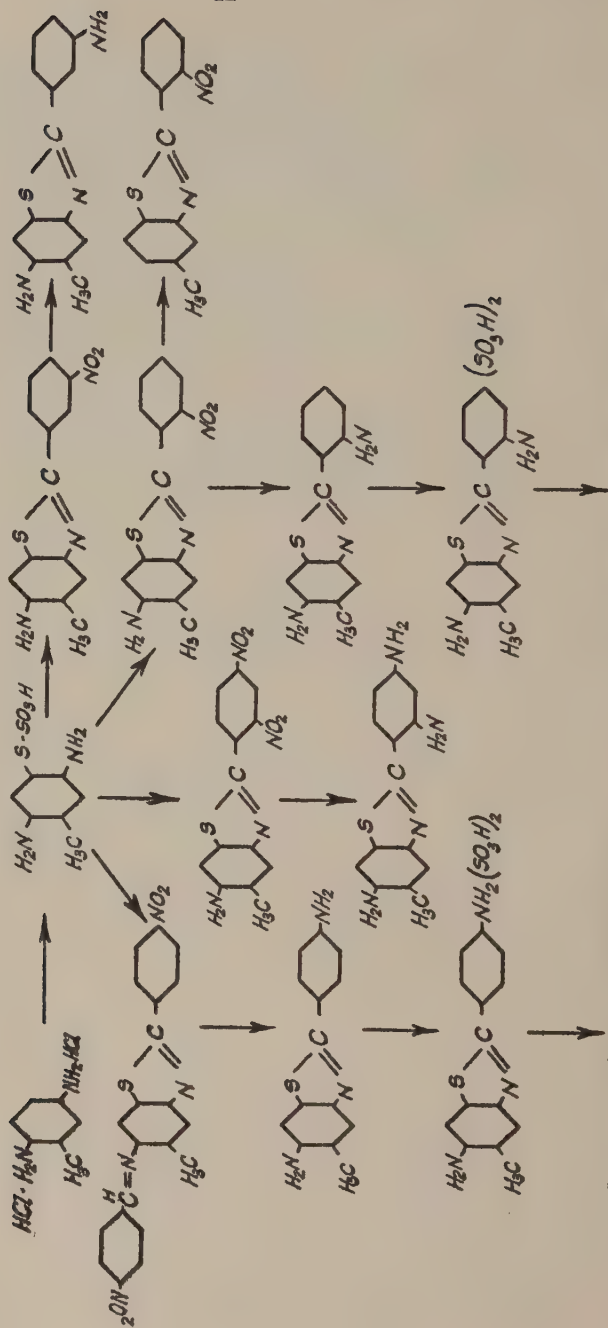
During the course of this investigation the following new compounds were prepared:

- (a) 1-methyl-benzene-2:5-diamino-4-thiosulfuric acid
- (b) 2-(o-nitrophenyl)-5-methyl-6-amino-benzothiazole
- (c) 2-(m-nitrophenyl)-5-methyl-6-amino-benzothiazole
- (d) 2-(p-nitrophenyl)-5-methyl-6-(p-nitrobenzalamino)-benzothiazole
- (e) 2-(o:p-dinitrophenyl)-5-methyl-6-amino-benzothiazole
- (f) 2-(o-aminophenyl)-5-methyl-6-amino-benzothiazole
- (g) 2-(p-aminophenyl)-5-methyl-6-amino-benzothiazole
- (h) 2-(o:p-diaminophenyl)-5-methyl-6-amino-benzothiazole
- (i) 2-(o-aminophenyl)-5-methyl-6-amino-benzothiazole-sulphonic acid
- (j) 2-(p-aminophenyl)-5-methyl-6-amino-benzothiazole-sulphonic acid
- (k) Columbia Yellow dye resulting from (i)
- (l) Columbia Yellow dye resulting from (j)

FLOW SHEET



- 12 -



COLUMBIA YELLOW TYPE OF DYE

COLUMBIA YELLOW TYPE OF DYE

INTRODUCTION AND DISCUSSION

MONOTHIOSULFURIC ACIDS OF AROMATIC DIAMINES

P-amino-dimethyl-aniline-thiosulfuric acid.

The first synthesis of a thiosulfuric acid of an organic base seems to have been effected as far back as 1885. C. Roth¹ in the course of preparation of a sulphur dye, synthesized p-amino-dimethylaniline-thiosulfuric acid from dimethylaniline, as an intermediate product, without, however, isolating the acid thus formed.

Bernthsen² during his important investigation on the methylene blue and methylene red groups of dyes, also prepared this acid by treating a neutral salt solution of p-amino-dimethylaniline with aluminum sulphate, followed by sodium thiosulphate and potassium dichromate.

Wahl³ prepared p-amino-dimethylaniline-thiosulfuric acid from p-nitroso-dimethylaniline by treating the latter compound with a solution of sodium thiosulphate. p-Amino-dimethyl-aniline-thiosulfuric acid thus formed coincides with that obtained by Bernthsen. This method was used by Bogert and Updike⁴ during their researches on thiazoles.

Gustav Heller⁵, following the above method of Wahl, prepared 1-methyl-p-amino-o-ethyl-toluidine-4-thiosulfuric acid.

Preparation of several diamino-thiosulfuric acids was effected by Bernthsen⁶. They are p-aminodiethylaniline-thiosulfuric acid, tetramethyl-phenylene-diamine-thiosulfuric acid, p-phenylene-diamine-thiosulfuric acid, tetraethyl-phenylene-diamine-thiosulfuric acid, p-aminodimethyl-o-toluidine-thiosulfuric acid⁷, p-amino-diethyl-o-toluidine-thiosulfuric acid.

According to Bernthsen⁸ diamino-thiosulfuric acids can also be prepared from diamine mercaptans when they are treated with H_2SO_3 and O_2 together. One can also convert the zinc salt of mercaptan by means of H_2SO_3 and dichromate into diamino-thiosulfuric acid.

Bernthsen also found that diamino-thiosulfuric acids could be obtained from methylene red by mixing an aqueous solution of this substance with dilute ammonia or alkali.

Polythiosulfuric Acids of Diamines

Up to 1903 only monothiosulfuric acids had been described. Green and Perkin⁹ in the course of their research on sulfide blacks synthesized polythiosulfuric acids of diamines. For the preparation of di- and tetra-thiosulfuric acids of p-phenylene-diamine they employed the same method as that used by

Bernthsen, with the exception that a larger molecular proportion of sodium thiosulphate and a corresponding proportion of the oxidizing agent were employed. These investigators claim that it is possible in this way to replace by $-\text{S}-\text{SO}_3\text{H}$ groups all of the nuclear hydrogens in p-phenylene-diamine.

Enhanced Reactivity of Nuclear Hydrogens of the Substances Yielding Thiosulfuric Acids.

The literature fails to record not only any mention of either benzene-, toluene-, naphthalene-, aniline-, toluidine-, naphthylamine-thiosulfuric acids, but also of the diamino-thiosulfuric acids except those of p-diamines and alkylated p-diamines. After the synthesis of p-toluylene-diamine-thiosulfuric acid an attempt was made to synthesize the thiosulfuric acid of 2:4-diamino-toluene, but this attempt met with failure.

For the formation of organic thiosulfuric acids, it therefore seems necessary to have either a structure, such as p-diamines, whose nuclear hydrogens are present in a state of enhanced reactivity, or a structure that could lend itself easily to such a state during the reaction. But since directive influence is a manifestation of the relative rates of substitution in the several available positions in a benzene nucleus, and that conditions external to the molecule usually have little effect, it must be considered that in all cases mentioned above, in connection with the preparation of diamino-thiosulfuric acid, the amino and alkylated amino groups para with respect to each other have enhanced the reactivity of all the nuclear hydrogens to the extent of their being easily replaced. This consideration seems valid for the reason that unstable inorganic thiosulfuric acid, capable of existing only in dilute aqueous solution, cannot enter into a reaction that involves severe experimental conditions without being subject to disruption.

The assumption that quinonoid structure, which is considered to possess all of its nuclear hydrogens in a state of easy replaceability, is responsible for the easy introduction of $-\text{S}-\text{SO}_3\text{H}$ group into the benzene nucleus may serve to explain the formation of some of the organic thiosulfuric acids; but there are, however, tetraalkylated p-diamines which cannot be considered capable of assuming quinonoid structure. Therefore, in all the cases mentioned above, the groups already present in the benzene nucleus of the substances forming thiosulfuric acid seem to have caused the nuclear hydrogens to be easily replaceable.

General Properties of Diamino-thiosulfuric Acids

According to Bernthsen¹⁰ on treating with excess sodium hydroxide amino-dimethylaniline-thiosulfuric acid decomposes

yielding amino-dimethyl-aniline disulfide; also sulphurous and sulphuric acid. In the absence of air, sulphuric acid is the only acid produced in addition to the amino-dimethyl-aniline-disulfide.

On reducing this compound by means of zinc dust and hydrochloric acid, amino-dimethyl-aniline-mercaptan is obtained.

Bernthsen also studied the effect of iodine, ferric chloride, dichromate, mercuric chloride, copper sulphate, platinic chloride, sulphurous acid and fuming hydrochloric acid on diamino-thiosulfuric acid.

The properties of polythiosulfuric acids of diamines in many respects are similar to those of monothiosulfuric acids of diamines. On reduction with zinc dust and hydrochloric acid they yield polysulphydro-p-diamines; on condensing with organic anhydrides and aldehydes, benzothiazoles are obtained; the action of nitrous acid on p-phenylene-diamine-polythiosulfuric acid produces a stable bisdiazosulphide.

Thiosulfuric Acids: Inorganic and Organic.

It is well known that inorganic thiosulfuric acid has not been isolated; it only exists in dilute solution when a dilute weak acid is added to a solution of sodium thiosulphate. Likewise the acid salt of thiosulfuric acid corresponding to NaHS_2O_3 has not been prepared. When, however, Na in the hypothetical NaHS_2O_3 or the H of the sulphydryl group in HSSO_3H is replaced by an organic diamine base, such as p-phenylenediamine, a stable organic thiosulfuric acid is obtained in crystalline form certain of whose properties, in spite of such a transformation, are more or less similar to those of the unstable inorganic thiosulfuric acid.

Preparation of 2:5-diamino-toluene-thiosoulfuric acid.

This acid was used exclusively as the starting material in this investigation, i.e., for the synthesis of the thiazole dye intermediates. This acid had not been prepared before. For its preparation p-toluylene-diamine was used as the basic material. The extremely unstable nature of this substance and the experimental difficulties involved in obtaining it in sufficient quantity were major problems to be faced at the beginning of this investigation. However, a generous quantity was obtained from the Fales Chemical Company.†

After reviewing the standard methods used for the preparation of thiosulfuric acids of diamines, and after carrying on

† We are greatly indebted to Fales Chemical Company, Cornwall, N. Y. for donating all of the p-toluylene-diamine used in this investigation.

certain preliminary experiments the method employed by Bernthsen¹¹, for the preparation of p-phenylene-diamine-thiosulfuric acid was adopted for the preparation of this new acid. In order to obtain the pure acid it was necessary, however, to introduce certain modifications into the method. Bernthsen uses about twice the quantity of reagents required by theory. It was found during this investigation that most satisfactory results were obtained when, for 7 moles of diamine-hydrochloride, 7 moles of sodium thiosulphate and one mole of potassium dichromate were employed.

In addition to the above reagents it is essential to use about 50 grams of aluminium sulphate. The role of this reagent in the reaction is not understood. The various chemical properties of p-toluylene-diamine-thiosulfuric acid are identical with those characteristic to the group.

Proving the Position of $-S-SO_3H$ Group in the p-Toluylene-diamine-thiosulfuric Acid.

There are three available ortho positions in the benzene nucleus of p-toluylene-diamine into which $-S-SO_3H$ group may enter. If the $-S-SO_3H$ group is situated at position (3) the condensation product with o-nitrobenzaldehyde will be 2-(o-nitrophenyl)-4-methyl-6-amino-benzothiazole; if at (4), it would yield 2-(o-nitrophenyl)-5-methyl-6-amino-benzothiazole; and if at (6) it would yield 2-(o-nitrophenyl)-7-methyl-6-amino-benzothiazole. If we diazotize the last three products and replace the diazo group by hydrogen, the resulting products would respectively be 2-(o-nitrophenyl)-4-methyl-benzothiazole, 2-(o-nitrophenyl)-5-methyl-benzothiazole, and 2-(o-nitrophenyl)-7-methyl-benzothiazole. Of the last three compounds the first has not yet been prepared; the second and the third have been prepared by Bogert and Allen.

On condensing the above acid with o-nitrobenzaldehyde we obtained a yellow substance. On diazotizing this compound and replacing the diazo group with hydrogen, we obtained shiny light yellow needle shaped crystals whose melting point and percentage of nitrogen checked with the calculated value for nitrogen, and the melting point for 2-(o-nitrophenyl)-5-methyl-benzothiazole. Therefore the thiosulfuric acid group must be situated at position (4) and the condensation product with o-nitrobenzaldehyde must be 2-(o-nitrophenyl)-5-methyl-6-amino-benzothiazole.

Potentiometric Titration of p-Toluylene-diamine-thiosulphuric Acid.

In order to measure the strength of diamino-thiosulphuric acid, titrations were carried out by means of 0.0202 Normal NaOH, and the results obtained were expressed graphically.

In the course of titration it was noticed that, after reaching a certain stage in the experiment, the potential begins to drop to a final equilibrium which is much lower than the initial potential. This phenomenon occurs only within a definite range P_H 7.66, (.6988 volt) to P_H 9.58 (.8124 volt). These figures represent the initial readings. Final equilibrium corresponding to P_H 7.66, after 75 minutes was 7.51 (or 0.6908 volt), and that corresponding to P_H 9.58 after twelve hours was 9.36 (or 0.7993 volt). The drop of potential takes place at every point within this range after the addition of sodium hydroxide. (See titration curve, page 31). The drop of potential is a minimum at either of these two points, and maximum at P_H 8.71 (or 0.7612 volt). The final equilibrium corresponding to P_H 8.71 is P_H 7.97 (or 0.7177 volt), after 30 hours a drop of 0.74 P_H unit (or 0.0435 volt).

The final neutralization equilibrium is easily attained at all points corresponding to measurements up to P_H 7.66 (or 0.6988 volt), and above P_H 9.58 (or 0.8124 volt).

The phenomenon within the above mentioned range may be due to one of the following causes:

(1) Decomposition of p-toluylene-diamine-thiosulfuric acid liberating sulphuric acid,

(2) Poisoning of the electrode by some impurity present in either thiosulphuric acid or sodium hydroxide,

(3) Liberation of hydrochloric acid occluded by the electrode during the process of platinizing in chloroplatinic acid, and the occluded diamino-thiosulfuric acid into which the electrode is immersed.

Due to the somewhat unstable nature of the diamino-thiosulfuric acids when in solution, one may be led to assume that along the neutralization region a maximum degree of instability is reached, and therefore the acid begins to decompose liberating free sulphuric acid, thus causing the fall of potential. If such a decomposition took place it should continue to break down, particularly in the alkaline region till it is completely transformed into its degradation products. In such a case the curve will assume an entirely different shape from this point on, and a new stoichiometrical relationship will be established. It can be seen from the results that after waiting 63 hours the final equilibrium remained constant, and the curve plotted from them is continuous and smooth.

Furthermore, if such a decomposition took place the solution should contain sulfuric acid and yield barium sulphate on the addition of $BaCl_2$. Addition of barium chloride produced no precipitate, showing that no decomposition had taken place.

A second possible cause is the poisoning of the electrode. There could be two sources responsible for this effect. (1) Diamino-thiosulfuric acid itself, and (2) some impurity present in sodium hydroxide. The fact that the curve proceeds smoothly, and the equilibrium is attained instantly at all points except within the neutralization region; and also the smoothness and continuity of the part of the curve passing through this region is against any possibility of poisoning of the electrode.

In order to substantiate the conclusions drawn above, the solution was titrated back with 0.0202 Normal HCl solution with the idea that if the above conclusions were correct the titration curve thus obtained should follow the same path as the final equilibrium curve, and possess the same shape and smoothness. The experiment proved that this is the actual fact, for the curve almost overlaps the previous one. Furthermore, the electrode, after standing 80 hours in the solution, was used to measure the potential of a freshly prepared thio-sulphuric acid solution of the same concentration as used in the above experiment. This potential was 0.4860 volt against 0.4923 volt; the latter value was obtained at the beginning of the experiment when the electrode was used for the first time. This result demonstrates the fact that the electrode has not suffered appreciable change during the experiment.

A third possible cause is the liberation of the hydrochloric acid occluded by the electrode during the process of platinizing in chloroplatinic acid solution and the p-toluylene-diamine-thiosulfuric acid occluded by the electrode during the period before reaching the neutralization region. In order to determine whether the electrode contributed to the occurrence of this phenomenon a new electrode was platinized under similar conditions and used to titrate 25 cc. of 0.1 Normal hydrochloric acid solution diluted to 125 cc. with distilled water. The steady neutralization equilibrium was obtained immediately at each point and no indication of drop of the potential could be observed during the entire course of titration. The curve plotted from the results was a typical hydrochloric acid titration curve. However, due to the fact that in the measurements of hydrogen-electrode potentials in inorganic solutions which are strongly acid, strongly alkaline, or well buffered, it is difficult to observe this phenomenon¹². It was necessary to study the measurements of the hydrogen-electrode potentials of an organic acid whose ionization constant approximated that of p-toluylene-diamine-thiosulfuric acid.

According to Ostwald¹³, K_a for propionic acid from the con-

ductivity measurements is $1.34 \times 10^{-6} \pm$. One hundred cc. of 0.0052 Normal propionic acid was titrated by means of 0.0197 Normal sodium hydroxide solution. The results are tabulated on page 32. In the course of the titration it was noticed also in this case that after reaching a certain point in the titration, the potential begins to drop to a final equilibrium which is much lower than the initial potential. This drift of potential occurs within the range of P_H 7.85 (.7104 volt) to 8.91 (.7730 volt). The final reading of potential corresponding to .7104 is .6504, a drop of 0.0170 volt. Beyond this point if any drift of potential is noticed it is upward in trend. A comparison of these results with those obtained from the measurements of the hydrogen-electrode potentials of p-toluylene-diamine-thiosulfuric acid will at once show a close resemblance and point to a common cause. Beans and Hammett¹⁷ from their studies on the hydrogen electrode conclude that the greatest single cause of this phenomenon is the overwhelming tendency of platinum to occlude substances of an acid nature and to give up the occluded acid slowly but continuously. Therefore in the light of observations made by Beans and Hammett, the phenomenon observed in this investigation may be attributed to the occlusion of acids. The molecular weight calculated from the stoichiometrical point of the final equilibrium curve is the one that approximates most satisfactorily the true molecular weight. This relationship is suggestive of the possibility of diamino-thiosulfuric acid having been occluded by the electrode to a greater extent than the hydrochloric acid from the chloroplatinic acid solution during the process of platinizing the electrode.

Ionization Constant of p-Toluylene-diamine-thiosulfuric Acid.

In the titration of p-toluylene-diamine-thiosulfuric acid the a weak acid 50% neutralized by a strong base is equal to the ionization constant of the acid provided the salt is practically completely ionized. In other words, the middle point of the titration curve of a particular acid lies near a point where the hydrogen ion concentration is numerically equal to the dissociation constant¹⁸.

In the titration of p-toluylene-diamine-thiosulfuric acid the middle portion of the titration curve corresponds to 10.65 cc, sodium hydroxide, or P_H 5.64, or $C_H = 5.56 \times 10^{-6}$. Hence $K_a = 5.56 \times 10^{-6}$.

‡ From the conductivity measurements at 25° C. ionization constant for propionic acid, according to White and Jones¹⁴, is 1.4×10^{-5} ; Franke¹⁵ 1.3×10^{-5} ; Drucker¹⁶ 1.3×10^{-5} . The shape of the titration curve plotted from our measurements is similar to that of acetic acid with an ionization constant of 1.86×10^{-5} .

Following the preparation and studying the properties of p-toluylene-diamine-thiosulfuric acid, attempts were made to synthesize a new group of thiazole dye intermediates with an ultimate object of converting them into new Columbia Yellow type of dyes.

SYNTHESIS OF NEW COLUMBIA YELLOW DYE INTERMEDIATES

Bogert and Bergeim¹⁹ during their investigation on the structure of Columbia Yellow Dye found that the methyl groups were essential only to deepen the shade. Columbia Yellow, lacking the methyl groups, was a paler yellow than the real Columbia Yellow, but still retained the property of fastness to cotton. They further showed that the amino group on the 2-phenyl part of the molecule was essential to color formation.

Following the work mentioned above, Bogert and Allen were interested in ascertaining just what effect on shade a methyl group would have if occupying one of the other possible positions in the benzothiazole portion of the Columbia Yellow molecule. They obtained dyestuffs from 2-(p-aminophenyl)-5-methyl-benzothiazole and of 2-(p-aminophenyl)-7-methyl-benzothiazole. These dyestuffs were found to be almost identical with Columbia Yellow in physical, chemical, and tinctorial properties. Both were found to dye cotton directly and dyeings were comparable to those with Columbia Yellow itself as regards fastness to acids, alkalies, light, and chlorine. Their final conclusion was that the position of the methyl group in the benzothiazole nucleus has very little effect on the shade of color produced.

They also studied the influence of the position of the amino group on the (2-phenyl) portion of the molecule by converting the dehydrothio-p-toluidines to thioflavine-T type of dyestuffs. From their studies of comparative dyeings they observed that the position of the NH_2 group did have a decided effect on the color. The brilliant, deep, greenish yellow color produced on silk by the para isomers and their behavior upon after-treatment with dilute sulphuric acid was materially altered when the NH_2 group was shifted to the other positions. A decided decrease in intensity of color resulted when the amino group occupied the ortho position: instead of a brilliant, deep greenish yellow the dyeings were of a pronounced paler tint; much of the fluorescent appearance had likewise been lost.

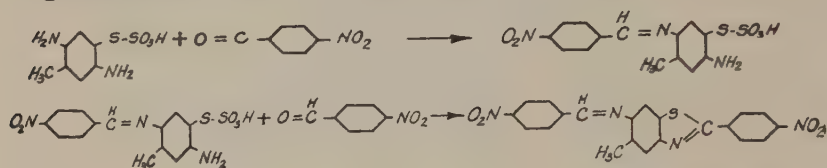
Our object was to study the effect of an amino group on Columbia Yellow when introduced into the benzothiazole nucleus, also to study the changes produced by shifting the position of the amino group in the (2-phenyl) portion of the molecule, and the problems incidental to such an investigation.

In order to achieve this objective we condensed 1-methyl-benzen-2:5-diamino-thiosulfuric acid with *o*-, *m*-, *p*- and 2:4-dinitro benzaldehydes in glacial acetic acid to obtain 2-(*o*-, *m*-, *o*:*p*-dinitro-phenyl)-5-methyl-6-amino-benzothiazoles. On reducing these products corresponding amino derivatives were obtained. The latter on sulphonation and alkaline hypochlorite oxidation yielded dyestuffs orange-tan in shade, yet similar to Columbia Yellow in physical, chemical and tinctorial properties. These differences will be discussed further at length in the latter part of this study.

During this investigation 2-(*o*-nitrophenyl)-5-methyl-6-amino-benzothiazole, 2-(*m*-nitrophenyl)-5-methyl-6-amino-benzothiazole, 2-(*o*:*p*-dinitrophenyl)-5-methyl-6-amino-benzothiazoles were easily obtained. But persistent attempts to obtain 2-(*p*-nitrophenyl)-5-methyl-6-amino-benzothiazole failed. Instead the 2-(*p*-nitrophenyl)-5-methyl-6-(*p*-nitrobenzal-amino)-benzothiazole was always obtained from the reaction. In this connection it is interesting to note that during the synthesis of 2-(*o*-nitrophenyl)-, and 2-(*m*-nitrophenyl)-isomers no evidence of the formation of corresponding benzalamino compounds was obtained. The reaction mixtures, after separating this product, 2-(*p*-nitrophenyl)-5-methyl-6-(*p*-nitrobenzal-amino)-benzothiazole, were subjected to repeated fractional crystallization, in the hope that these mixtures contained some of the 2-(*p*-nitrophenyl)-5-methyl-6-amino-benzothiazole isomer. In no case were we successful. The ease of the formation of 2-(*p*-nitrophenyl)-5-methyl-6-(*p*-nitrobenzal-amino)-benzothiazole from *p*-toluylene-diamine-thiosulfuric acid and *p*-nitrobenzaldehyde with the formation of practically no 2-(*p*-nitrophenyl)-5-methyl-6-amino-benzothiazole, and the fact that the sole products from the condensation of the acid and *o*-nitro-, and *m*-nitro-benzaldehydes are 2-(*o*-nitro-, or *m*-nitrophenyl)-5-methyl-6-amino-benzothiazoles presents to us a problem of interest, and an attempt to explain this difference might be of theoretical value.

It seems that when *p*-nitro-benzaldehyde is condensed with *p*-toluylene-diamine-thiosulfuric acid either both of the amino groups in the latter reagent react simultaneously with two molecules of the former, yielding 2-(*p*-nitrophenyl)-5-methyl-6-(*p*-nitrobenzal-amino)-benzothiazole, or the reaction proceeds in two steps. In the latter case the reaction takes place be-

tween the ortho-amino group and p-nitrobenzaldehyde first, yielding p-nitro-benzalamino-m-toluidine-thiosulfuric acid, then the second reaction between m-amino group and benzaldehyde followed by the thiazole ring closure. The two-step reaction may be shown to take place according to the following scheme:



Whereas in condensing the o-nitro-, and m-nitrobenzaldehydes with the acid, the reaction prior to the thiazole ring closure appears to take place entirely at the amino group which is para to the ortho amino group. Once the thiazole ring is closed there appears to be no reaction between the free amino group in the ortho position and the excess ortho and meta nitrobenzaldehydes.

Unsuccessful Attempts to Hydrolyze Benzalamino Condensation Product.

After failing to obtain the 2-(p-nitrophenyl) isomer by direct synthesis, it was hoped that by hydrolyzing the benzalamino compound with mineral acids it would be possible to liberate the desired substance. Therefore, the benzalamino compound was refluxed with dilute sulfuric and concentrated hydrochloric acid, but the hydrolysis of this compound could not be effected even after long periods of refluxing. Similar treatment with dilute nitric acid attacks the benzal derivative producing a light orange colored amorphous substance incapable of crystallization. Concentrated nitric acid nitrates it in the cold within two minutes, yielding a new nitro compound of purplish orange color. Here we have a benzalamino compound which resists the most drastic form of benzalamino hydrolysis.

On reducing, however, the benzal-amino condensation product yielded 2-(p-amino-phenyl)-5-methyl-6-amino-benzothiazole. The product obtained, however, was the amino and not the nitro compound.

2-(Aminophenyl)-aminobenzothiazoles are obtained by reducing 2-(nitrophenyl)-amino-benzothiazoles by means of tin and hydrochloric acid. They all are soluble in alcohol from which they crystallize out in the form of fine needles. The color they possess and the fluorescence they manifest in alcoholic solution vary considerably from one isomer to another. Furthermore they show *dichroism*.

With the exception of 2-(m-aminophenyl)-5-methyl-6-amino-benzothiazole they were easily obtained, and their properties determined. The above isomer, however, could not be obtained in pure crystalline form. The substance obtained by first crystallization has an olive color. It was not sufficiently pure, however, to obtain a sharp melting point, and for the analysis for carbon and hydrogen. Subsequent attempts at crystallization result in transforming the compound into a deep green colored amorphous substance incapable of crystallization.

During the process of crystallization it was noticed that some of the substances in this series crystallize out in the form of needle shaped crystals of two different colours. At first it was thought that the different colours represented different substances but on determining mixed melting points and analyzing, they were found to be the same compound. The compounds which manifested dichroism are 2-(o:p-dinitrophenyl)-5-methyl-6-amino-benzothiazole, 2-(o-nitrophenyl)-5-methyl-6-amino-benzothiazole, 2-(o-aminophenyl)-5-methyl-6-amino-benzothiazole, 2-(p-aminophenyl)-5-methyl-6-amino-benzothiazole.

Columbia Yellow Type Dyes.

For practical and theoretical reasons, of the several dehydrothio-toluidines prepared during this investigation, 2-(o-aminophenyl)-, and 2-(p-aminophenyl)-, isomers were sulphonated and subjected to alkaline hypochlorite oxidation in order to obtain the dyes corresponding to these amines.

Columbia Yellow is obtained by the oxidation of the only amino group present in the 2-phenyl portion of the dehydrothio-p-toluidine into an azo group. But the dehydrothio-p-toluidines that we used possess two amino groups. The question, therefore arises whether one or both of the amino groups might be transformed into the azo group to give the above dyes. In order to clear this point it was necessary to diazotize the dyes and couple the reaction product with β -naphthol to see if it gave a new substance different in color. By carrying on this experiment we obtained a decidedly red solution, which dyed unbleached cotton tan, possessing a red tint. This experiment seems to indicate that one of the two amino groups exists intact in the molecule.

Comparative Study of the Color of Constitutionally Similar Thiazole Dyes and Dye Intermediates.

Not only the color of the above new dyes was found to be decidedly deeper and different in shade than the Columbia Yellow dyes obtained by previous investigators, but the new isomers of dehydrothio-toluidines manifested a decided change

in color on shifting the amino group present in the phenyl nucleus, the thiazole nucleus remaining constant. When the amino group occupied the ortho position the substance possessed a red violet or yellow shade. Shifting the amino group to the meta position made the shade deeper. Similarly when the amino group occupied the para position there appeared a different shade and depth of color.

Bogert and Allen synthesized dehydrothio-p-toluidines corresponding in every respect to those we have prepared except that the former lacked the additional amino group in the thiazole nucleus. They are 2-(o-aminophenyl)-5-methyl-benzothiazole, yellow; 2-(m-aminophenyl)-5-methyl-benzothiazole; purplish white; and 2-(p-aminophenyl)-5-methyl-benzothiazole, yellow. When these isomers are compared among themselves we notice that the shifting of the position of the amino group in the 2-phenyl portion of the molecule does not appear to produce appreciable changes in color. The new isomers that we have prepared are 2-(o-aminophenyl)-5-methyl-6-amino-benzothiazole, yellow shade 1 and red violet shade 1; 2-(p-aminophenyl)-5-methyl-6-amino-benzothiazole, yellow orange shade 2, greenish yellow medium, 2-(m-aminophenyl)-5-methyl-6-amino-benzothiazole, greenish yellow shade 2, and green. A glance at the color of these isomers brings into prominence the influence of the amino group when shifted to various positions.

On the other hand when we compare the members of the first group prepared by Bogert and Allen, with the members of the second group prepared by us, we notice that 2-(o-aminophenyl)-5-methyl-6-amino-benzothiazole has red violet shade 1 color against the yellow color of 2-(o-aminophenyl)-5-methyl-benzothiazole. 2-(m-Aminophenyl)-5-methyl-6-amino-benzothiazole has yellow, shade 2, or green against pinkish white color of 2-(m-aminophenyl)-5-methyl-benzothiazole; and 2-(p-aminophenyl)-5-methyl-6-amino-benzothiazole has yellow orange shade 2, or greenish yellow medium color against light yellow color of 2-(p-aminophenyl)-5-methyl-benzothiazole.

On comparing the nitro derivatives of the first group with the corresponding derivatives of the second group we notice also appreciable differences in depth and shade of color. 2-(o-Nitrophenyl)-5-methyl-6-amino-benzothiazole has orange yellow or greenish yellow shade 1, against the light yellow color of 2-(o-nitrophenyl)-5-methyl-benzothiazole; 2-(m-nitrophenyl)-5-methyl-6-amino-benzothiazole has yellow orange, normal tones against the white colored needles of 2-(m-nitrophenyl)-5-methyl-benzothiazole. Unfortunately, as mentioned above it has been impossible to obtain 2-(p-nitrophenyl)-5-methyl-6-amino-benzothiazole to compare with the corresponding

homolog in which one amino group in the thiazole nucleus is absent.

Another interesting point can be brought about from the above comparisons. When light yellow 2-(o-nitrophenyl)-5-methyl-benzothiazole is reduced to yellow 2-(o-aminophenyl)-5-methylbenzothiazole, and white colored 2-(m-nitrophenyl)-5-methyl-benzothiazole to purplish white 2-(m-aminophenyl)-5-methyl-benzothiazole, the transformation from nitro to amino derivatives does not seem to produce appreciable difference in color, whereas when greenish yellow shade 1, 2-(o-nitrophenyl)-5-methyl-6-amino-benzothiazole is reduced to red-violet shade 1, 2-(o-aminophenyl)-, and yellow orange, normal tones, 2-(m-nitrophenyl)-5-methyl-6-amino-benzothiazole reduced to the green-colored amino derivative, the transformation from nitro to amino compounds produces considerable difference in color and depth.

These conclusions drawn from the above comparisons can be attributed to the presence of the amino group situated in position 6 in the thiazole nucleus.

It would be interesting if a direct comparison could have been made between the true Columbia Yellow and the new ones obtained in connection with this investigation, but due to the difference in position of the methyl group in each case an exact comparison could not be made at present. However, the experimental results obtained by Bogert and Allen can be taken to indicate that the above conclusions may apply also to this case. According to their findings sulphonation and alkaline-hypochlorite oxidation of 2-(p-aminophenyl)-5-methyl-benzothiazole and of 2-(p-aminophenyl)-7-methyl-benzothiazole yielded dyestuffs almost identical with Columbia Yellow in physical, chemical and tinctorial properties. Both dyed cotton directly and dyeings were comparable to those with Columbia Yellow itself as regards fastness to acids, alkalies, light, and chlorine. Comparative dyeings of these isomers showed that the position of the methyl group in the benzothiazole nucleus has very little effect on the shade of color produced. When the methyl group occupied No. 5 position the color was deepest; when it occupied No. 7 position the color was lightest of the three. The differences among these shades of yellow were so very slight that it was concluded that, at least in this series of dyestuffs, the position of the methyl group exerted very little effect on depth of shade.

EXPERIMENTAL

1. 2:5-Diamino-1-methyl-benzene-4-thiosulfuric acid.

50 grams of 2:5-diamino-toluene hydrochloride²⁰ dissolved in 120 cc. of water was treated with 50 grams of powdered aluminium sulphate. To this mixture 64 grams of sodium thiosulphate dissolved in 120 cc. water was added by constant stirring. When this cold solution was added to the above mixture a thick white precipitate developed, due probably to the formation of diaminothiosulphate²¹. This was followed by the addition of 120 cc. of dichromate solution containing 10 grams of potassium dichromate. The addition of the dichromate solution must be carried out in small quantities within a minute by constant stirring. The solution assumed first a green, and finally dark purplish-green color. After a few minutes it was filtered through a coarse filter paper by means of a Buchner funnel. The filtrate, after standing 6 to 10 hours, yielded a small amount of dark red amorphous substance, this was filtered out and the filtrate was left to stand for 48 to 72 hours, after which period the diamino-thiosulfuric acid crystallized out in the form of dark steel-gray rhombic crystals; yield 15%.

Purification. The crystals obtained as above were not sufficiently pure for analytical purposes. The purification was best effected by grinding it in a mortar and suspending it first in alcohol, and then in ether for several hours. This operation was repeated until the alcohol and the ether filtrates were nearly colorless. The organic impurities produced in the reaction as side products were thus removed. Further purification was effected by washing several times with slightly warm water and suspending in citric acid solution to remove the iron that might be present as an impurity in the toluylene-diamine hydrochloride. The iron, if present in the latter substance, was dragged down and held firmly by the diamino-thiosulfuric acid. It was possible to remove it only by the above process of purification.

Melting-Point. This substance on ignition in a porcelain crucible swelled up and burned without passing through the stage of fusion; therefore the melting point could not be determined.

Analysis for carbon, hydrogen and sulphur:

Sample, .2577 g.; water .1017 g.; CO₂ .3390 g.

Found: H = 4.42% C = 35.88%

Calc. for C₇H₁₀N₂O₃S₂ H = 4.27% C = 35.88%

Sample .2290 g.; BaSO₄ .4593 g.

Found: S = 27.64% Calc. S = 27.40%

Attempts were made to prepare this compound in large quantities by a single batch, but the products thus obtained were not of pure quality, and the yield was low. Therefore for the preparation of a large quantity of this substance it was necessary to run several small batches at a time.

2. Proving the position of $-S-SO_3H$ group in the nucleus of p-tolylene-diamine.

Since there were available three ortho positions, namely, 3, 4, 6 in the diamine into which $-S-SO_3H$ group could enter, it was necessary to prove its exact position. To this end this acid was condensed with o-nitro-benzaldehyde in the presence of glacial acetic acid. The product thus obtained after purification was diazotized and the diazo group replaced by hydrogen²².

One-half gram of the above substance was treated with 2 cc. of concentrated HCl, 2 cc. of water and 5 grams of ice. This mixture was immersed in an ice bath and diazotized by adding 0.8 gram of sodium nitrite dissolved in 5 cc. of water. The reaction mixture, after standing thirty minutes in the ice bath, was filtered and the precipitate suspended in 30 cc. of concentrated formic acid and exposed to sunlight for three hours. On refluxing this mixture for ten minutes and pouring it into water, a light yellow substance separated out. This product was purified by crystallizing it from 60% alcohol in the form of shiny light yellow needles, m.p. 91.5-92.0°C (Corr.) This melting point corresponds exactly to that of 2-(o-nitro-phenyl)-5-methyl-benzothiazole prepared by Bogert and Allen to which reference has already been made.

Analysis:

Calc. for $C_{14}H_{10}O_2N_2S$: S = 10.37%. Found: N = 10.59%

Sample 3.871 mgs.

Vol. of N at 26° C and 760 mm. press (Corr.) 0.359 cc.

The $-S-SO_3H$ group therefore is present at position 4, and must have a constitution corresponding to 2:5-diamino-1-methyl-benzene-4-thiosulfuric acid.

3. Unsuccessful attempt to prepare 2:4-diamino-1-methyl-benzene-thiosulfuric acid.

An attempt was made to prepare the thiosulfuric acid of 2:4-diamino-toluene²³ employing exactly the same method outlined above for the preparation of 2:5-diamino-1-methyl-benzene-4-thiosulfuric acid, but this attempt was met with failure. A small amount of substance that separated out from the reaction mixture was inorganic in nature, and experiments

to discover the presence of a trace of this acid yielded negative results. It was refluxed with nitrobenzaldehydes in the presence of acetic acid, but the reaction mixtures did not show the characteristic color changes due to the condensation products resulting from nitrobenzaldehydes and diamino-thio-sulfuric acids.

4. Potentiometric titration of 2:5-diamino-1-methyl-benzene-4-thiosulfuric acid.

One hundred milligrams of substance was suspended in 100 cc. of distilled water in a 100 cc. volumetric flask and was dissolved by shaking. The solution was transferred to a hydrogen gas electrode vessel made of pyrex glass. The flask was rinsed with 25 cc. of water and added to the main solution. This cell was connected to the saturated calomel electrode by means of a glass stoppered salt bridge filled with saturated potassium chloride solution. The titration was carried out at 25° C. by means of a Type K potentiometer in an atmosphere of hydrogen, which was purified by passing over heated copper oxide. The air was excluded from the system by an air tight set up.

The calomel electrode and the hydrogen electrode were controlled by determining potentiometrically the PH of a 0.104 Normal HCl solution. The calculated PH of a 0.104 Normal HCl is 1.01. The observed PH of a 0.104 Normal HCl is 1.01. The observed PH from the potentiometric measurements was 0.99.

The measured E.M.F. values were converted to PH values by employing the formula:

$$\log_{10} \frac{1}{C} = \frac{E \text{ (observed)} - E \text{ (calomel)}}{0.00019837 T} = P_H$$

The numerical value of the saturated KCl calomel electrode used in this formula was 0.2461 volt at 25°C.

The stoichiometrical point was 21.3 cc. of 0.0202 Normal NaOH. For the reasons expressed in the introduction the titration was reversed by 0.0202 Normal HCl. The results of these two titrations are given below.

Table I

(A) Titration of 2:5-diamino-1-methyl-benzene-4-thiosulfuric acid by means of 0.0202 Normal NaOH.

Ccs. of NaOH added	Time Increments		E.M.F.	P _H
	hrs.	min.		
00.00		30	0.4923	4.16
.95		15	0.5075	4.42
2.50		10	0.5268	4.73
5.00		10	0.5475	5.10
7.50		10	0.5629	5.36
9.00		5	0.5711	5.49
10.00		5	0.5760	5.58
10.75		5	0.5800	5.64
12.00		5	0.5866	5.75
14.00		5	0.5977	5.94
16.00		5	0.6109	6.17
19.00		5	0.6449	6.74
19.50		5	0.6558	6.93
20.00		5	0.6751	7.25
		15	0.6735	
		25	0.6725	
	2		0.6690	7.16
20.2		5	0.6767	7.28
		30	0.6759	7.27
20.5		5	0.6988	7.66
	1	10	0.6908	7.51
20.75		5	0.7404	8.19
		15	0.7351	
	9		0.7013	7.70
21.10		5	0.7612	8.71
		30	0.7572	
		30	0.7444	
	28	5	0.7177	7.97
21.50		5	0.7945	9.27
		10	0.7891	
	2		0.7757	8.96
22.00		5	0.8124	9.58
	6		0.8059	9.47
	6		0.7993	9.36
23.00		5	0.8366	9.99
		25	0.8363	

Table I Cont'd

Ccs. of NaOH added	Time Increments		E.M.F.	P _H
	hrs.	min.		
24.00		5	0.8535	
		30	0.8535	10.27
26.00		5	0.8701	
		20	0.8702	10.55
28.00		5	0.8797	10.72
		15	0.8810	10.74
30.00		5	0.8872	
		10	0.8872	10.84
32.00		5	0.8917	
		10	0.8917	10.92

Table II

(B) Reversing the titration (A) by means of 0.0202 Normal HCl

Ccs. of HCl added	Time Increments		E.M.F.	P _H
		min.		
00.00		00	0.8917	10.92
2.14		10	0.8847	10.80
4.66		5	0.8732	10.61
7.26		20	0.8538	10.28
8.28		5	0.8384	10.02
9.33		10	0.8135	9.43
9.85		11	0.7884	9.17
10.36		10	0.7257	8.10
11.60		7	0.6635	7.06
12.43		5	0.6412	6.68
13.46		30	0.6263	6.43
14.50		12	0.6153	6.24
15.54		8	0.6069	6.10
17.61		42	0.5931	5.87
19.68		8	0.5801	5.65
21.75		15	0.5703	5.48
23.83		12	0.5588	5.29
25.90		6	0.5460	5.07
27.97		13	0.5314	4.82
30.04		5	0.5097	4.46
32.00		17	0.4850	4.04

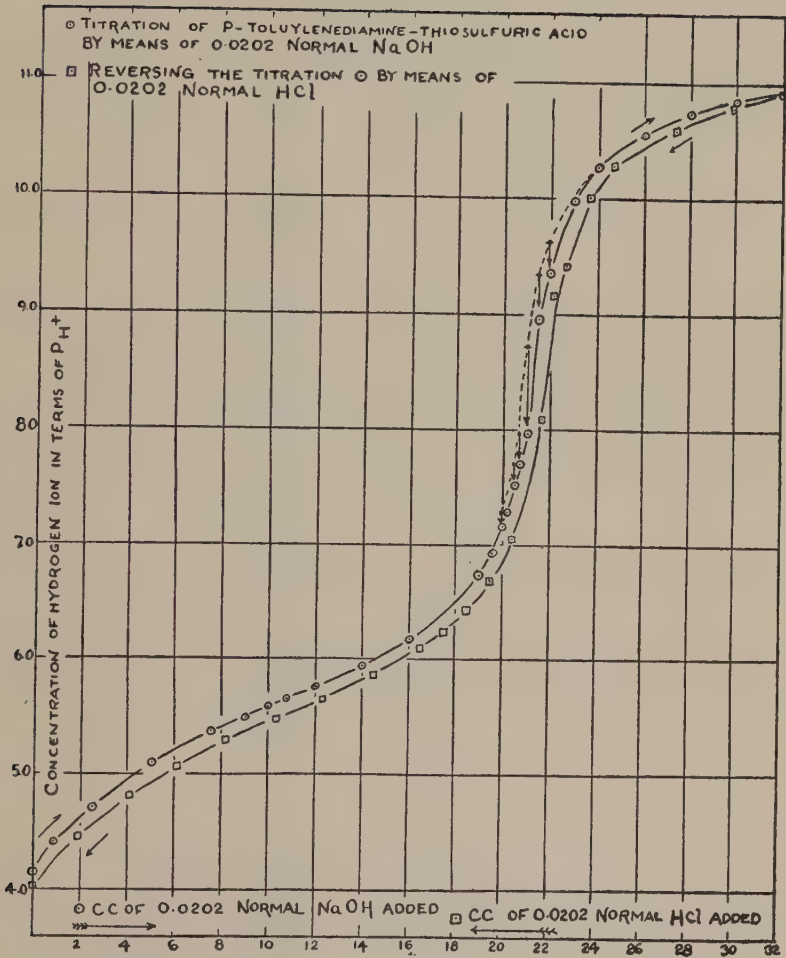


Table III

POTENTIOMETRIC TITRATION OF 100 cc. of 0.0052 NORMAL
PROPIONIC ACID BY MEANS OF 0.0197 NORMAL
NaOH SOLUTION

Ccs. of NaOH added	Time Increments		E.M.F.	P _H
	hrs.	min.		
00.00		30	.4553	3.53
1.65		7	.4691	
		9	.4718	
		5	.4718	3.82
4.65		6	.4895	
		7	.4892	
		4	.4893	4.11
9.65		5	.5054	
		5	.5054	4.38
14.65		8	.5352	
		4	.5350	
		5	.5352	4.89
19.65		5	.5553	
		5	.5563	
		5	.5562	5.24
22.30		6	.5742	
		5	.5742	5.55
24.00		4	.5994	
		5	.5994	5.97
24.65		5	.6150	
		5	.6150	6.24
25.15		8	.6460	
		6	.6460	6.76
25.40		7	.7104	7.85
		10	.7172	
		18	.6787	
		15	.6632	
		8	.6600	
	2	45	.6504	6.84
		15	.6500	
25.95		7	.7730	8.91
		13	.7730	
	6	10	.7560	
		10	.7560	8.62
26.65		4	.8135	9.60
	2	14	.8235	

Table III Cont'd

Ccs. of NaOH added	Time Increments		E.M.F.	P _H
	hrs.	min.		
27.65		8	.8240	9.77
		3	.8460	
		15	.8492	
29.65		5	.8492	10.20
		3	.8685	
		5	.8710	
32.00		5	.8710	10.57
		3	.8825	
		45	.8817	

Experiments for the presence of SO_4 ion in the titrated solution.

In order to find out whether diamino-thiosulfuric acid underwent any decomposition during the titration producing sulphuric acid, the following experiment was carried out. At first a control test was run as follows: a freshly prepared 0.1% diamino-thiosulfuric acid solution was treated with an excess of 5% barium chloride solution. The solution, after standing 24 hours, was filtered and the residue, after ignition in a platinum crucible, weighed 0.0002 gram. This result shows that the diamino-thiosulfuric acid gives practically no sulphate ion. Another solution of similar concentration first titrated to P_H 9.9. then acidified with HCl was treated as above, and the residue obtained weighed 0.0004 gram against 0.0066 gram of BaSO_4 calculated on the basis of acidity produced within the neutralization region. It therefore seems that no sulphuric acid has been produced during the titration.

5. 2-(o-Nitrophenyl)-5-methyl-6-amino-benzothiazole.

To ten grams of p-toluylene-diamine-thiosulfuric acid 8 grams of o-nitro-benzaldehyde²⁴ and 80 cc. of glacial acetic acid were added. This mixture was refluxed first mildly for 20 to 30 minutes and then strongly for one hour. The mixture assumed dark red appearance as the temperature of the reaction mixture rose. During the process of refluxing considerable bumping developed due to the formation of an insoluble cream colored substance, which was possibly the acetate of the desired product. The mixture was filtered by means of suction while hot, and more of the precipitate separated from the filtrate as the latter cooled and was added to the original precipitate. Treating this precipitate with caustic soda and heating on a water bath, this cream-colored substance was changed to a

yellow solid. Seven grams of the former gave 5 g. of the latter, which proved to be the compound sought.

On diluting the filtrate with a small amount of water till a slight precipitate was produced, and evaporating down by passing a stream of compressed air over the solution almost all of the desired substance separated out, which was purified by crystallizing from 90% alcohol. The crystals were orange yellow and greenish yellow, shade 1, needles; m.p. 143.9°C. (Corr.), yield 36%. These crystals in alcohol showed a suggestion of purplish red fluorescence.

Analysis: Sample .1823 g.; water .0650 g.; CO₂ .3921 g.;

Found: H = 3.99%; C = 58.86%

Sulphur: Sample .2438 g.; BaSO₄ .2021 g.; Found: S = 11.38%

Calc. for C₁₄H₁₁O₂N₂S: H = 3.86%; C = 58.94%; S = 11.24%

The final filtrate was composed of tarry materials and other unstable intermediate products, which darkened and decomposed on drying even at ordinary temperature.

6. 2-(m-Nitrophenyl)-5-methyl-6-amino-benzothiazole.

A mixture of 10 grams of p-toluylene-diamine-thiosulfuric acid, 8 grams of m-nitro-benzaldehyde²⁵ and 80 cc. of glacial acetic acid was refluxed gently for 20 to 30 minutes, then for one hour with a moderate flame. Violent heating was avoided. The temperature of the mixture during refluxing rose to 116° to 118° C. It assumed a dark red appearance as the temperature rose. There was noticed slight bumping but this was essentially due to the formation of some decomposition product which separated out. At the end of the reaction period the solution was filtered while hot by means of suction. The filtrate on cooling yielded the major portion of the desired substance due to its sparing solubility in cold glacial acetic acid. The filtrate was then diluted with water sufficient to produce moderate turbidity; excess water was avoided to prevent the precipitation of the tarry materials, etc. On heating the turbid solution, the undesired tarry substance went into solution, leaving the desired product in more or less pure state. This substance was best purified by refluxing it in a large volume of glacial acetic acid and charcoal to get rid of the tarry impurities, and finally it was crystallized from toluene. The crystallization from toluene took place slowly. The crystals were yellow orange colored fine needles; m.p. 233.5°C. (Corr.); yield 58.5%; manifested yellowish red fluorescence in toluene.

Analysis: Sample: .1991 g.; water .0710 g.; CO₂ .4282 g.

Found: H = 3.99% C = 58.76%

Calc. for C₁₄H₁₁O₂N₂S: H = 3.86% C = 58.94%

7. 2-(p-Nitrophenyl)-5-methyl-6-(p-nitro-benzalamino)-benzothiazole instead of 2-(p-nitrophenyl)-5-methyl-6-amino-benzothiazole.

A mixture of 11 grams of p-toluylene-diamine-4-thiosul-

furic acid, 15 grams of p-nitrobenzaldehyde²⁶ and 75 cc. of glacial acetic was refluxed, first gently, for thirty minutes, and then for one hour with a moderate flame. The solution assumed dark-red color immediately and began bumping, due partly to some decomposition product and partly to the formation of a dark-red insoluble substance. At the end of the reaction the mixture was filtered hot. The precipitate was soluble only in hot xylol from which it crystallized out in the form of dark red fine needles with a melting point of 279° C. (Corr.). The filtrate on treating with alcohol and heating on steam bath yielded more of this substance due to its insolubility in alcohol-acetic acid mixture. The product thus obtained was sufficiently pure because of the solubility of the other side products in the double solvent. This dark red substance manifested greenish-yellow fluorescence in xylol. It was first taken for 2-(p-nitrophenyl)-5-methyl-6-amino-benzothiazole, but the analytical results for carbon and hydrogen were confusing. Therefore it was again analyzed several times; all the results were perfect checks. In order to learn the constitution of this new compound it was analyzed also for nitrogen and sulphur.

Analysis for C, H, N, S.

Sample, .1769 g.; water .0616 g.; CO₂ .3892 g.; H = 3.91%; C = 60.00%

" .1916 g.; water .0675 g.; CO₂ .4226 g.; H = 3.94%; C = 60.15%

" 4.320 mgs.; water 1.420 mgs.; CO₂ 9.540 mgs.; H = 3.68%;
C = 60.22%

" 3.316 mgs.; vol. N (Corr.) .384 cc.; T = 298° C;

V, P, = 758.2 mm. (Corr.) N = 13.24%

" .1731 g.; BaSO₄ .0968 g.; S = 7.67%

Calc. for C₂₂H₁₄O₄N₂S, C = 60.30%; H = 3.32%; S = 7.65%; N = 13.4%

The empirical formula calculated from the above results is
C_{20.91}H_{15.1}O_{3.96}N_{3.96}S₁.

Molecular weight determination of the above substance.

The molecular weight of the above substance was determined by the depression of the freezing point using phenol as solvent. 0.175 g. and 0.1710 g. substance was dissolved in 21.600 g. and 21.500 g. phenol respectively. The depression of the freezing point for the first quantity was 0.150°C. and 0.145°C. for the second; which gave a molecular weight of 405.1 and 411.4 against the calculated molecular weight of 418, with an average error of 2.2%.

After separating the above identified substance, the rest of the several reaction mixtures was subjected to a systematic fractional crystallization to obtain 2-(p-nitro-phenyl)-5-methyl-6-amino-benzothiazole. As the result of several attempts a few very small fractions were obtained, their melting point ranged from 260° to 315°C. The last fraction weighed 0.005 g.; m.p. 312 to 315°C. Bright orange colored fine needles.

Analysis: Sample: 2.783 mgs.; water 0.742 mg.; CO₂ 5.890 mgs.

Found: H = 3.00% C = 57.72%

Calc. for C₁₁H₁₁O₂N₂S: H = 3.86% C = 58.94%

Several other synthetic attempts were made to obtain this substance by varying the molecular proportion of p-nitro-benzaldehyde and the thiosulfuric acid, but benzalamino compound was invariably the resulting product.

8. Unsuccessful attempts to hydrolyze 2-(p-nitrophenyl)-5-methyl-6-(p-nitro-benzalamino)-benzothiazole.

Ordinarily the condensation products between an amine and aldehyde hydrolyze by refluxing with dilute acid yielding the original substances. Several attempts to hydrolyze the above substance by means of acids, however, failed utterly. In each case the original substance was quantitatively recovered. This substance was refluxed with 30% sulphuric acid and concentrated hydrochloric acid for several hours without being able to disrupt the combination between the amine and the carbon of the aldehyde group. The attempt to hydrolyze this combination with nitric acid solutions of different strengths resulted in decomposing the compound.

9. Effect of reduction on 2-(p-nitrophenyl)-5-methyl-6-(p-nitro-benzalamino)-benzothiazole.

On reducing this substance by means of tin and hydrochloric acid, the benzalamino combination was severed; the reduction product being, however, 2-(p-aminophenyl)-5-methyl-6-amino-benzothiazole instead of 2-(p-nitrophenyl)-5-methyl-6-amino-benzothiazole which we were attempting to obtain.

10. 2-(p-Nitrophenyl)-5-methyl-6-(p-nitro-benzalamino)-2-nitro-benzothiazole.

With the hope of breaking the benzalamino combination with concentrated nitric acid it was treated as follows:

1 gram of 2-(p-nitrophenyl)-5-methyl-6-(p-nitro-benzalamino)-benzothiazole was treated with 25 cc. conc. nitric acid in the cold for one to two minutes. On diluting the reaction mixture with water, a nitration product was obtained. It was crystallized from xylol in the form of red orange (normal tones) colored fine needles, which melted at 247.6°C. (Corr.) then congealed and remained unmelted at 300°. The product was apparently an impure mononitro derivative of the p-nitro-benzalamino compound.

Analysis: Sample: 3.740 mgs.; water 1.140 mgs.; CO₂ 7.438 mgs.

Found: H = 3.41%, C = 54.24%

In order to form an idea with respect to the position of this additional NO_2 group 50 mgs. of this new substance were reduced by means of tin and hydrochloric acid. The resulting product was too small to purify further for a melting point determination and analysis for carbon and hydrogen.

13. 2-(*o*-Dinitrophenyl)-5-methyl-6-amino-benzothiazole.

Ten grams of *p*-toluylene-diamine-4-thiosulfuric acid, 15 grams of 2:4-dinitrobenzaldehyde (the preparation of this was carried out according to the method outlined by Sachs and Kempf²⁷ and 80 cc. of glacial acetic acid were refluxed, first gently for 30 minutes and then with a moderate flame to boiling for one hour. It was then filtered hot. A small amount of the acetate was obtained as an insoluble product. On treating the latter product with alkali the desired substance was obtained. By evaporating down the filtrate by means of a stream of compressed air and adding alcohol to the concentrated solution, a precipitate was obtained from which the above desired substance was obtained. Purification of this from a hot benzene solution gave the desired product in the form of red, (normal tones), or red (shade 1, violet tint) colored fine needles; m.p. 239.2°C . (Corr.); yield 30%. It manifested greenish fluorescence in benzene.

Analysis: Sample: .1778 g.; water .0496 g.; CO_2 .3327 g.
 Found: H = 3.12% C = 51.03%
 Calc. for $\text{C}_{14}\text{H}_{10}\text{O}_4\text{N}_4$; H = 3.03%; C = 50.90

14. 2-(*o*-Aminophenyl)-5-methyl-6-amino-benzothiazole.

Four grams of 2-(*o*-nitrophenyl)-5-methyl-6-amino-benzothiazole dissolved in 25 cc. of concentrated hydrochloric acid were gently refluxed with 10 grams of tin for 2 hours. The reaction mixture was filtered to remove the excess tin. The filtrate was diluted with an equal volume of water and made strongly alkaline by means of a strong sodium hydroxide solution, and allowed to cool. The precipitate was made into a paste again in a mortar by means of sodium hydroxide solution to break the tin-amine combination. The free impure amine was crystallized out from 65% alcohol in the form of yellow, shade 1, or red-violet shade 1 needles. It manifested bluish violet fluorescence in alcoholic solution; m.p. 251°C . (Corr.); yield 70%.

Analysis: Sample: 4.647 mgs.; water, 2.185 mgs.; CO_2 , 11.155 mgs.,
 " 4.110 " " 1.915 " " 9.890 "
 Calc. for $\text{C}_{14}\text{H}_{11}\text{N}_3\text{S}$: H = 5.13%; C = 65.88%
 Found: H = 5.25% C = 65.47%
 5.21% 65.63%

15. 2-(m-Aminophenyl)-5-methyl-6-amino-benzothiazole.

Four grams of 2-(m-nitrophenyl)-5-methyl-6-amino-benzothiazole were treated after the method outlined above. But unlike the o-aminophenyl isomer all attempts to obtain this substance in a pure crystalline form for melting point determination and for carbon and hydrogen analysis proved fruitless. The first crystallization from 65% alcohol yielded yellow, shade 2, fine needles, melting around 218°C , but further attempts at purification caused the compound to undergo some transformation which likewise could not be purified. This form was soluble in water with a deep green color. The substance obtained by first crystallization manifested greenish-blue fluorescence in alcohol.

16. 2-(p-Aminophenyl)-5-methyl-6-amino-benzothiazole from 2-(p-nitrophenyl)-5-methyl-6-(p-nitro-benzalamino)-benzothiazole.

3.0 grams of substance, 50 cc. of concentrated HCl, and 6 grams of granulated tin were refluxed for 3 hours. The clear liquid was then filtered, diluted with an equal volume of water and made strongly alkaline by means of a concentrated NaOH solution. The resulting product was made into a paste in a mortar by means of a sodium hydroxide solution, filtered, and washed. The substance crystallized from 50% alcohol in the form of yellow orange, shade 2, or greenish yellow (medium) needles; m.p. 255.5°C . (Corr.). It possessed purplish fluorescence in alcoholic solution.

Analysis: Sample: 3.580 mgs.; water 1.673 mgs.; CO_2 8.664 mgs.

Found: H = 5.22%; C = 65.98%

Calc. for $\text{C}_{14}\text{H}_{13}\text{N}_2\text{S}$ H = 5.13%; C = 65.88%

17. 2-(o:p-Diamino-phenyl)-5-methyl-6-amino-benzothiazole.

One gram of 2-(o:p-dinitrophenyl)-5-methyl-6-amino-benzothiazole, 4 grams of granulated tin and 35 cc. of conc. HCl were treated as outlined for No. 14. The amino compound crystallized from 50% alcohol as orange, shade 2, fine needles. It manifested sky blue fluorescence in alcoholic solution; m.p. 285.5°C . (Corr.); yield 70%.

Analysis: Sample: 3.329 mgs.; water 1.595 mgs.; CO_2 7.581 mgs.

Found: H = 5.36%; C = 62.11%

Calc. for $\text{C}_{14}\text{H}_{14}\text{N}_4\text{S}$: H = 5.18%; C = 62.22%

18. 2-(o-Aminophenyl)-5-methyl-6-amino-benzothiazole-sulphonic acid.

Two grams of No. 14 were treated with 15 cc. conc. sulphuric acid and 20 grams of 50% fuming sulphuric acid and heated over a water bath at $60-70^{\circ}\text{C}$. for ten hours²⁸. It was then poured on cracked ice and the precipitate filtered, which

was then dissolved in ammonia, precipitated by hydrochloric acid a few times and dried at 120°C.

Analysis:

Sample: 0.1052 g.; H₂O 0.0360 g.; CO₂ 0.1542 g.; H = 3.83%; C = 40.08%

Calc. for C₁₁H₁₁N₃S (SO₃H)₂ H = 3.13%; C = 40.48%,

Calc. for C₁₁H₁₂N₃S (SO₃H) H = 3.88%; C = 50.14%

If the sulphonation were carried out at lower temperatures, a mixture of mono- and di-sulphonic acids was obtained which could not be separated because of their solubility in water to the same extent.

19. 2-(p-Aminophenyl)-5-methyl-6-amino-benzothiazole-sulphonic acid.

Two and a half grams of No. 16 were treated with 20 cc. conc. sulphuric acid and 25 grams of 50% fuming sulphuric acid and heated for fifteen hours over a water bath at 75 to 85°C.²⁹ The purification was carried out after the method used in No. 18.

Analysis for Carbon and Hydrogen:

Sample:

4.611 mgs.; H₂O 1.565 mgs.; CO₂ 6.950 mgs.; H = 3.82%; C = 41.10%

Sample:

5.190 mgs.; H₂O 1.830 mgs.; CO₂ 7.770 mgs.; H = 3.94%; C = 40.83%

Analysis for Sulphur:

Sample: 6.440 mgs.; BaSO₄ 8.965 mgs.; S = 19.16%

Sample: 6.697 mgs.; BaSO₄ 9.980 mgs.; S = 20.5%

Calc. for C₁₄H₁₁N₃S (SO₃H)₂ H = 3.13%; C = 40.48%; S = 23.13%,

Calc. for C₁₄H₁₂N₃S (SO₃H) H = 3.88%; C = 50.14%; S = 19.16%.

From the percentage of carbon, the above analyses seem to show that the products are disulphonic acids; however, the results for hydrogen and sulphur indicate that they are a mixture of mono- and disulphonic acid. Due to the fact that melting point determination cannot be employed to study the purity of sulphonic acids, and also because of the solubility of the above mono- and disulphonic acids in water to the same extent, it has not been possible to obtain a sufficiently pure product for analysis.

20. A New Columbia Yellow Type of Dye from 2-(o-aminophenyl)-5-methyl-6-amino-benzothiazole.

This dye was obtained by dissolving No. 18 in sodium carbonate solution and treating with a freshly prepared NaOCl solution and allowing it to stand for 24 hours. The solution immediately assumed deep dark red. At the end of 24 hours it was found more satisfactory to acidify with conc. hydrochloric acid to precipitate the dye. It was then filtered and the precipitate was dissolved in ammonia and precipitated by hydrochloric acid. It was then subjected to crystallization by dissolving in water and reprecipitating with conc. hydrochloric acid. The product obtained by a second precipitation

was dissolved in water and evaporated to dryness on a watch glass over a steam bath. During this operation the dye dried out in the form of threads which resembled needle-shaped crystals of shiny dark black color. The threads were easily detached by means of a spatula. The impurities dried above and below this circulatory striated portion of the dried mass.

Analysis:

Sample:

4.575 mgs.; water 1.360 mgs.; CO_2 7.757 mgs.; $\text{H} = 3.33\%$; $\text{C} = 46.02\%$

Sample:

4.390 mgs.; water 1.237 mgs.; CO_2 7.352 mgs.; $\text{H} = 3.15\%$; $\text{C} = 45.67\%$

Calc. for $\text{C}_{28}\text{H}_{18}\text{N}_6\text{S}_2 (\text{SO}_3\text{H})_4$ $\text{H} = 2.66\%$; $\text{C} = 40.67\%$

Calc. for $\text{C}_{28}\text{H}_{20}\text{N}_6\text{S}_2 (\text{SO}_3\text{H})_2$ $\text{H} = 3.34\%$; $\text{C} = 50.45\%$

21. A New Columbia Yellow Type of Dye from 2-(p-aminophenyl)-5-methyl-6-amino-benzothiazole.

One half gram of 2-(p-aminophenyl)-5-methyl-6-amino-benzothiazole sulphonic acid was converted to Columbia Yellow type of dye according to the method outlined in No. 20.

Analysis:

Sample: 5.668 mgs.; water 1.335 mgs.; CO_2 9.332 mgs.

Found: $\text{H} = 2.63\%$; $\text{C} = 44.90\%$

Calc. for $\text{C}_{28}\text{H}_{18}\text{N}_6\text{S}_2 (\text{SO}_3\text{H})_4$ $\text{H} = 2.66\%$; $\text{C} = 40.67\%$

Calc. for $\text{C}_{28}\text{H}_{20}\text{N}_6\text{S}_2 (\text{SO}_3\text{H})_2$ $\text{H} = 3.34\%$; $\text{C} = 50.45\%$

While these dyes were prepared from the amino sulphonic acids, whose analyses indicated that they were disulphonic acids, subsequent analyses of the dyes showed that the latter were a mixture of di- and tetra-sulphonic acids of Columbia Yellow. However, due to the fact that the sulphonic acids practically have no influence on the tinctorial properties of the dyes, for our theoretical discussion the tinctorial properties of the dyes will be the same regardless of whether they are the pure di- or tetra-sulphonic acids or a mixture of the two.

22. Dyeing experiments with the dyes obtained from 2-(o-amino-phenyl)-5-methyl-6-amino-benzothiazole, and 2-(p-amino-phenyl)-5-methyl-6-amino-benzothiazole.

All of the dyeing experiments with the above Columbia Yellow type of dyes during this investigation were carried out according to the method outlined by Bogert and Bergeim³⁰.

2 grams of unbleached cotton

40 cc. of 0.1% aqueous dye solution

50 cc. of water

8 drops of 10% sodium carbonate solution

30 cc. of 1% sodium chloride solution

Heated 30 to 45 minutes on a boiling water bath. The un-

bleached cotton was soaked in water by digesting in boiling water prior to the dyeing experiments. Unmordanted unbleached cotton was dyed a shade of orange tan color. The dye resulting from the 2-(p-aminophenyl)-isomer possessed the deeper tint of the two. Fastness of the dyeings was made by the method outlined by Knecht, Rawson and Lowenthal³¹.

22. Coupling of the new dyes with β -Naphthol.

Due to the fact that Columbia Yellow was obtained by the oxidation of the amino group to $-N=N-$ and the fact that 2-(o-aminophenyl)- and 2-(p-aminophenyl)-5-methyl-6-amino-benzothiazoles contained two free amino groups, it was important to learn whether one or both of these groups suffered oxidation to an azo group. To study this question the dyes were diazotized according to the usual method and coupled with β -naphthol in an alkaline solution. The solution got deep dark brown-red immediately, indicating that coupling had taken place. This mixture was used to dye a piece of unbleached cotton; the cotton dyed a tan color possessing a red tint. This seems to show that there is present only one azo group in the molecule, and the amino groups in the benzothiazole nuclei remain intact.

SUMMARY

A method for the preparation of 1-methyl-benzene-2:5-diamino-4-thiosulfuric acid is described. The ionization constant of this acid from the potentiometric titration curve is calculated to be 5.56×10^{-6} at 25° C. Potentiometric titration was also carried out on propionic acid to correlate certain similar facts observed in both cases.

An explanation is offered to account for the easy introduction of $-S-SO_3H$ group into the aromatic p-diamines and alkylated p-diamines.

On condensing p-toluylene-diamine-thiosulfuric acid with o-, m-nitro- and o:p-dinitrobenzaldehydes corresponding thiazoles are formed, but on condensing p-nitrobenzaldehyde with this acid 2-(p-nitrophenyl)-5-methyl-6-(p-nitro-benzalamino)-benzothiazole is the main product. An attempt has been made to present a probable mechanism of reaction to account for the formation of the last mentioned product. Attempts to hydrolyze this product have met with failure.

On reducing the 2-(o-nitrophenyl)-compound the corresponding 2-(o-amino-phenyl)-compound has been obtained. It has not, however, been possible to obtain 2-(m-aminophenyl)-5-methyl-6-amino-benzothiazole in pure form by this method. Attempts at the purification of the reduced product of the 2-(m-nitrophenyl)-compound have caused it to undergo unidentifiable transformations; this has been attributed to its possible unstable nature. Para isomer of 2-(o-aminophenyl)-compound has been obtained by the reduction of 2-(p-nitrophenyl)-5-methyl-6-(p-nitrobenzalamino)-benzothiazole.

2-(o-amino-, and p-animophenyl)-5-methyl-6-amino-benzothiazoles are converted into their sulphonic acids and the latter are changed to Columbia Yellow type of dyes. These new dyes have been diazotized and coupled with β -naphthol to demonstrate the existence of free amino groups in these dyes. Dyeing experiments are carried out on these new dyes. A comparative study of color is made among the constitutionally similar thiazole dyes and dye intermediates prepared during this investigation and those prepared by the previous investigators.

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BIOGRAPHICAL

Manasseh G. Sevag was born in Sis, Cilicia, Armenia, September 16, 1897. He received the degree of Bachelor of Arts in 1920 from St. Paul's College (American College), Tarsus, Cilicia. He was a graduate student at Yale University during 1920-21; and in the biochemistry and bacteriology department of The New York Post Graduate Medical School during 1922-23. Biochemist to Flower Hospital, New York City, 1923-24. Graduate student, Chemistry Department, Columbia University 1924-26; lecture assistant in this department during 1925-26 and laboratory assistant since 1927. Research Chemist with the Fales Chemical Company since July 1926. He is a member of the American Chemical Society, Sigma Xi honorary scientific society, and New York Academy of Sciences.

